

## ALD precursor chemistry: Evolution and future challenges

M. Leskelä and M. Ritala

Department of Chemistry, University of Helsinki, P.O. Box 55, 00014 Helsinki, Finland

**Abstract:** The requirements of ALD precursors differ from those of CVD concerning thermal stability, adsorption on the surface, and reactions towards each other. In the first ALD experiments in the 70s elements (Zn, Cd, S), metal halides and non-metal hydrides ( $H_2O$ ,  $H_2S$ ) were used. In the 80s the selection of precursors widened to metal complexes (alkoxides,  $\beta$ -diketonates) and simple organometallics (alkyl compounds). In the 90s both new metal (Cp-compounds, alkylamides) as well as non-metal precursors ( $H_2O_2$ ,  $O_3$ , hydrazine) have been introduced. A characteristic feature of ALD is that surface groups play an important role as reactive sites for the next precursor pulse. The development of ALD precursors is limited by the small number of groups working in the field. It seems, however, that the precursor development is diverged and tailored molecules are designed for each process.

### 1. INTRODUCTION

Atomic Layer Deposition (Epitaxy) developed in the early 70s is a modification of CVD and can also be called as "alternately pulsed-CVD" [1,2]. Gaseous precursors are introduced one at a time to the substrate surface and between the pulses the reactor is purged with an inert gas or evacuated. In the first reaction step the precursor is saturatively chemisorbed at the substrate surface and during the subsequent purging the excess of the precursor is removed from the reactor. In the second step the other precursor is introduced on the substrate and the desired film growth reaction takes place. After that the reaction byproducts and the precursor excess are purged out from the reactor. When the precursor chemistry is favourable, *i.e.* the precursors adsorb and react with each other aggressively, one ALD cycle can be performed in less than one second in properly designed flow type reactors.

The striking feature of ALD is the saturation of all the reaction and purging steps which makes the growth self-limiting. This brings the large area uniformity and conformality, the most important properties of ALD, as shown in very different cases, *viz.* planar substrates [3], deep trenches [4] and in the extreme cases of porous silicon [5] and high surface area silica and alumina powders [6,7]. Also the control of film thickness is straightforward and can be made by simply calculating the growth cycles. ALD was originally developed to manufacture luminescent and dielectric films needed in electroluminescent displays [8] and a lot of effort has been put to the growth of doped zinc sulfide and alkaline earth metal sulfide films [9]. Later ALD has been studied for the growth of different epitaxial III-V [10,11] and II-VI [12,13] films, non-epitaxial crystalline or amorphous oxide [14,15] and nitride [16,17] films and their multilayer structures. Minor attention has been given to grow other films like those of metals and fluorides [18]. There has been considerable interest towards the ALE growth of silicon and germanium films but due to the difficult precursor chemistry the results have not been very successful [19,20].

### 2. REQUIREMENTS FOR THE ALD PRECURSORS

The precursors maybe gaseous, liquid or solid and in the last two cases the requirement is that they must be volatile. The vapor pressure must be high enough for effective mass transportation. The solids and some

liquids need to be heated inside the reactor and introduced through heated tubes to the substrates. The necessary vapor pressure must be reached at a temperature below the substrate temperature to avoid the condensation of the precursors on the substrate.

The self-limiting growth mechanism of ALD makes it easy to use also relatively low vapor pressure solids precursors though their evaporation rates may somewhat vary during the process because of changes in the surface area. The technologically challenging task of pulsing precursors evaporated at high temperatures is solved elegantly by inert gas valving [2,3]. A challenge remaining with very small particle size solids is how to prevent the particles from being transported by the carrier gas and entering the films.

The precursors must be thermally stable at the substrate temperature because their decomposition would destroy the surface control and accordingly the advantages of the ALD method. A slight decomposition is slow compared to the ALD growth, is acceptable as shown in the case of metal alkoxide precursors in the growth of oxide films [21,22].

The precursors have to chemisorb on or react with the surface. The interaction between the precursor and the surface as well as the mechanism of the adsorption is different for different precursors as will be pointed out later on. The adsorption can in the most cases be considered as an exchange reaction as reported in the growth of oxide films where the surface OH groups play an important role [23,24]. After purging the molecule at the surface has to react aggressively with the second precursor and form the desired solid film. The demand of highly reactive precursors in ALD is in marked contrast to the selection of precursors in conventional CVD. The aggressive reactions guarantee effective use of precursors, short pulse times and purity of the films in ALD. Thermodynamic considerations of the film formation reactions are useful although the dynamic conditions in the process do not completely fulfill the real equilibrium requirements. An aggressive reaction desired means that reactions having large negative values of  $\Delta G$  are looked for. Unfortunately programs for calculations exist [25] but unfortunately thermodynamic data are not available for a large number of organometallic precursors. The  $\Delta G$  value is only tentative since it tells about the spontaneity of the reaction between the gaseous precursor molecules but nothing on the kinetics and, more importantly, nothing on adsorption. If there is no site where the precursors can adsorb and be anchored, the growth will not take place. There is no thermodynamic data for calculation and prediction of adsorption and surface reactions and therefore to get predictions of them extensive quantum chemical calculations are needed. The requirement for a negative  $\Delta G$  is not strict since the growth proceeds under dynamic conditions where by-products are removed from the surface. The reaction between  $\text{InCl}_3$  and water to  $\text{In}_2\text{O}_3$  has been successfully utilized in ALD although its  $\Delta G$  is slightly positive [26].

The side-products in the reaction must be gaseous in order to allow their easy removal from the reactor. The side-products should not further react or adsorb on the surface. The reaction between metal chlorides and water, often used in the ALD growth of oxide films, produces HCl which may readsorb or react and cause lowering of the growth rate or inhomogeneity in film thickness as shown in the case of Ti, for example [23,27,28]. HCl has been shown to adsorb also on the alumina and undergo an exchange reaction between the OH group, most readily with the basic ones [29].

Precursors should not react with the film and cause etching.  $\text{NbCl}_5$  is an extreme example since it reacts with niobium oxide and volatile oxochlorides are formed hindering the film growth [30].  $\text{TaCl}_5$  reacts slightly similarly but the etching is not so severe and  $\text{Ta}_2\text{O}_5$  film can be grown in a self-limiting manner at the temperature where the etching begins, about 275 °C [31].

The final requirement for the precursor is that it should not dissolve in the film. This rather rare case was observed when copper films were grown using zinc vapor as a reducing agent. Zinc dissolved in the forming brass. During purging and the next copper precursor ( $\text{CuCl}$ ) pulse zinc was re-evaporated and uncontrolled copper formation reaction took place [32].

While integrating ALD processes for making complete devices, the compatibility of the precursor with the underlying material, substrate or film, must be taken into account. No etching, harmful reactions or dissolution may take place.

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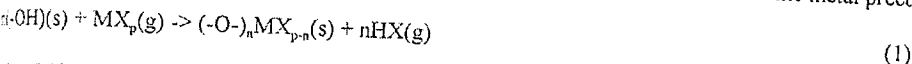
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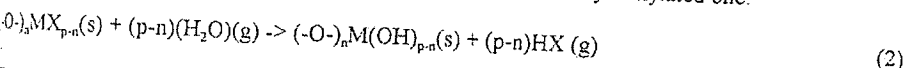
## 3. PRECURSOR COMBINATIONS AND SURFACE AS A REACTANT

The unique features of ALD are not that much reflected in the choices of single precursor molecules which are essentially the same as those used in CVD. Rather, it is the way how they are combined (Table 1) which makes the difference. As mentioned above, the precursors must react aggressively and completely. The difference to CVD chemistry is clear since ALD favours precursor combinations, for example trimethylaluminium (TMA) + water, zinc chloride + hydrogen sulfide, which in CVD can not be mixed together and introduced simultaneously into the reactor.

The surface chemistry of ALD relies on either molecular chemisorption or, perhaps more often, reaction of the incoming precursor with the functional group on the surface. Experimental evidences of the latter case have been reported in many papers on ALD oxide films using water as an oxygen precursor [17,23,24,33,34]. There the actual reaction takes place between the OH groups on the surface and the metal precursor:



where M is a metal ion, X is a ligand, typically halide, alkoxide or alkyl. p varies depending on the metal and ligand and n varies depending on the amount of surface hydroxyl groups which in turn is a function of temperature. During the next pulse water changes the surface to a hydroxylated one:



The correlation between the amount of hydroxyl groups on the surface and the amount of metal precursors adsorbed has been shown in the experiments made on high surface area silica powder [33]. Also the low growth rate of  $\text{In}_2\text{O}_3$  thin films, known to be deficient of surface OH groups, can be explained by the lack of reaction sites during the indium precursor pulse [34]. On the other hand, the increase of the water dose in a pulse significantly increases the growth rates of oxide films which can be understood in terms of increased hydroxyl group densities [35].

The lack of anchoring sites or functional groups can be the reason for the non-ideal results obtained for example with III-V compound and elemental (metal) films. On the other hand, ALD growth on selective sites could be utilized in selective area growth experiments by patterning the OH terminated surface and growing the film on the OH covered areas only. Crystallographically selective area growth is also possible as shown by Isshiki et al. [36,37]. They grew epitaxial III-V films and by controlling purging times they were able to deposit GaAs and GaP films either selectively on the (100) surfaces only or simultaneously on both the (100) and (111) surfaces of their (100)GaAs substrates which contained V-shaped grooves with the (111) oriented sidewalls.

Direct experimental evidences on molecular chemisorption in ALD are sparse. Real time quartz crystal microbalance (QCM) measurements can be used to monitor the relative masses of adsorbed species [38]. Most processes studied by this method involve metal chlorides and water precursors and are aimed for oxide films, and also in the studies on  $\beta$ -diketonato complexes water has been used as the oxygen precursor. Thus the effect of OH groups is present in the adsorption which involves partial release of the  $\beta$ -diketonato ligands [39,40]. Kawai and coworkers [41,42] have shown, however, that  $\text{Cu}(\text{thd})_2$  and  $\text{Ca}(\text{thd})_2$  can chemisorb on silica surface without exchange reaction via the interaction between surface oxygen atoms and C=O bonds in the complex.

## 4. PRECURSORS USED

The need to develop a new deposition method for electroluminescent (EL) thin film devices which require high-quality, pinhole-free dielectric and luminescent films deposited on large area glass substrates resulted in the discovery of the ALD method [8]. In the monochrome yellow-emitting EL devices  $\text{ZnS:Mn}$  thin films

are used as the phosphor material. Therefore, the first experiment carried out used elemental zinc and sulfur as precursors and that is the origin of the name Atomic Layer Epitaxy. When grown on single crystal substrate at high enough temperature, real epitaxy can be obtained. Soon it turned out that molecular precursors ( $\text{ZnCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{H}_2\text{S}$ ) are more convenient to handle and films of the quality needed in EL devices can be achieved. For these reasons and because only a few of them are volatile enough, elements are rarely used as precursors, II-VI compounds being the exceptions (Table 1). Epitaxial CdTe has been grown on (100) GaAs in a monolayer fashion at a limited temperature range (260-290 °C) and at higher temperatures 0.5 ML/cycle growth was achieved [43]. With ZnSe the process window for 1 ML/cycle is wider, viz. 250-350 °C [44]. The use of elemental zinc as a reducing agent in the ALD growth of transition metal nitrides is also worth mentioning [14,16,18].

In the following the ALD precursor chemistry is highlighted according to different precursor types. Table 1 summarizes the different precursors and reactions used in ALD without references. For detailed references the recent reviews [15,45,46] are referred to.

#### 4.1 Precursors for non-metals

##### 4.1.1 Oxygen

Water has been by far the mostly used precursor chemical for oxygen. It reacts fast with many metal halides and alkyls and reasonably well with metal alkoxides forming via surface hydroxyl groups oxide films as described above. Problems with water arise with  $\beta$ -diketonato complexes because the reaction does not occur or is slow at temperatures below 500 °C. In CVD  $\beta$ -diketonates have been used together with oxygen but usually the temperature has been rather high [47].  $\text{Y}_2\text{O}_3$  films are the only ones reported to be grown by ALD from  $\beta$ -diketonates ( $\text{Y}(\text{thd})_3$ ) and  $\text{O}_2$  with a low rate of 0.2 Å/cycle [48]. The inertness of the molecule can be explained by the double bond and accordingly all burning reactions need high temperatures. The use of ozone instead of oxygen makes the ALD growth of oxides from the  $\beta$ -diketonates faster but slightly non-ideal since no ALD-window can be found but the growth rate increases with increasing temperature [48,49].

$\text{H}_2\text{O}_2$  has been in few difficult cases ( $\text{In}_2\text{O}_3$ ,  $\text{SiO}_2$ ) used instead of water to improve the growth rate [50,51]. The improvement can be explained by the increased number of OH groups on the surface.  $\text{H}_2\text{O}_2$  reacts also with TMA more eagerly than water but at low temperatures the resulting  $\text{Al}_2\text{O}_3$  films are not as dense as is the case also when water is used [52]. Alcohols have been used as oxygen precursor in deposition of  $\text{Al}_2\text{O}_3$  films from both  $\text{AlCl}_3$  and different alkoxides [53].

##### 4.1.2 Sulfur and selenium

Hydrogen sulfide is a suitable and the mostly used sulfur precursor in ALD. It reacts well with very different metal precursors: halides, alkyls, carboxylates,  $\beta$ -diketonates and cyclopentadienyl compounds (Table 1).  $\text{H}_2\text{S}$  is used in the large scale production of ZnS based and pilot scale production of SrS based EL phosphors. Quantum chemical calculations on the reaction  $\text{ZnCl}_2 + \text{H}_2\text{S} \rightarrow \text{ZnS}$  have shown that the interaction of  $\text{H}_2\text{S}$  on  $\text{ZnCl}_2$  surface is dependent on the arrangement of the  $\text{ZnCl}_2$  molecules. Independently chemisorbed  $\text{H}_2\text{S}$  molecules favour additive reaction of  $\text{H}_2\text{S}$  and the critical step is the formation of HCl while  $\text{ZnCl}_2$  molecules favour the immediate reaction to ZnS [54,55]. A mass-spectroscopic study of the same reaction showed that HCl is released only after the  $\text{H}_2\text{S}$  pulse and not after the  $\text{ZnCl}_2$  pulse [56].

The reaction between dimethyl zinc and  $\text{H}_2\text{S}$  proceeds in a monolayer fashion at 250-310 °C [57]. The process is sensitive to  $\text{H}_2$  purge and  $\text{Zn}(\text{CH}_3)_2$  dose. It is proposed that dimethyl zinc adsorbs as a monolayer on the sulfur surface. The  $\text{H}_2$  sensitivity gives indications for the possibility of an inhibiting reaction.

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in ALD. It reacts well with very different cyclopentadienyl compounds (Table 1). the production of SrS based EL phosphors. nS have shown that the interaction of H<sub>2</sub>S. molecules. Independently chemisorbed ZnO. s the formation of HCl while ZnCl<sub>2</sub> changes. dic study of the same reaction showed the pulse [56]. nonolayer fashion at 250-310 °C [57]. It. d that dimethyl zinc adsorbs as a molecule. possibility of an inhibiting reaction when

metallic zinc and methane are formed [57]. A recent detailed study on Cd(CH<sub>3</sub>)<sub>2</sub> + H<sub>2</sub>S ALE reactions showed, however, that dimethyl cadmium chemisorbs dissociatively releasing methane and forming a monomethylated surface [58]. Methane is also released during the H<sub>2</sub>S pulse and a SH surface is formed. The mechanism proposed where the surface SH groups play an important role resembles closely to that reported for water and surface OH groups.

Hydrogen selenide reacts like hydrogen sulfide with zinc chloride and alkyl compounds forming ZnSe. The studies have been focused on verifying the ML growth/cycle and details of the mechanisms and the possible role of SeH groups have not been reported. The use of a thermal precursor cracker improves the film quality and has been explained by the formation of elemental species having surface mobility higher than Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and H<sub>2</sub>Se [59].

### 4.1.3 Nitrogen

Ammonia has automatically been the precursor for nitride films. Three types of approaches have been taken towards nitride films: epitaxial GaN (Al<sub>1-x</sub>Ga<sub>x</sub>N, Ga<sub>1-x</sub>In<sub>x</sub>N) films grown from alkyl compounds and ammonia for optoelectronic applications [60], polycrystalline AlN films for dielectric and passivation layers [61] and polycrystalline transition metal nitrides (TiN, NbN, TaN, Ta<sub>3</sub>N<sub>5</sub>, MoN) grown from metal chlorides for diffusion barrier and protective applications [14]. In systems where no reduction of the metal (Al, Ga, In) is needed ammonia works rather well. The impurities found from for example AlN films: chlorine and hydrogen with AlCl<sub>3</sub> [61,62] and carbon and hydrogen with TMA [62], show that ammonia leaves behind some hydrogen. The oxygen found in the AlN films is concentrated on the surface indicating post deposition oxidation. Volatile transition metal precursors usually contain metals at their highest oxidation states but in the nitrides the oxidation state is +III and therefore reduction must occur. Ammonia is reducing in nature and for example TiN can be prepared with the reaction between TiCl<sub>4</sub> and NH<sub>3</sub> and the film made at 500 °C is rather pure but films of better conductivity are obtained if zinc is used as an additional reducing agent [16]. Ammonia does not reduce TaCl<sub>5</sub> and Ta<sub>3</sub>N<sub>5</sub> is formed, and Zn vapour reduction is needed for TaN [63,64]. As a summary, ammonia is a suitable precursor for nitride formation reactions with metal chlorides if the metal ion has not to be reduced. If reduction is needed an additional reducing agent may be necessary. The situation may change if other metal precursors than chlorides are used as shown in the case of TiCl<sub>4</sub> [65].

### 4.1.4 Hydrides of Group V (15) Elements

PH<sub>3</sub>, AsH<sub>3</sub> and SbH<sub>3</sub> are the most common precursors for the group V elements. In ALE they have been used together with both chlorides and alkyl compounds of the group III elements (Table 1). The ALE growth of the III-V compounds has not been very successful because of the complexity of the surface chemistry and there is no single mechanism for the growth of the III-V compounds by ALE. The difficulties in the surface chemistry are believed to be mainly due to the group III precursors and not because of the group V hydrides. However, the As-H species play certainly an important role in the chemisorption of TMG and the instability of surface AsH<sub>3</sub> is a partial reason for the problems. Fast injection of AsH<sub>3</sub>, high hydrogen partial pressure and injection of atomic hydrogen on AsH<sub>3</sub> surface have improved the self-limiting type growth [45]. However, in some experiments wide temperature, pulse time and pressure windows have been observed [66] and they must be addressed to the ligand exchange reactions similar to those described for the growth of oxide films. The precursors for the group V elements are not under special development but the users are satisfied to the compounds commercially available for MOVPE.

#### 4.1.5 Fluorine

The only paper existing on the ALD of fluoride films reports the use of  $\text{NH}_4\text{F}$  as a precursor for Ca, Sr and Zn fluorides [67]. The precursor is not ideal and the growth rate remains low. In deposition of  $\text{SrS-CeF}_3$  fluoride codoping has been performed by benzoyl fluoride which is a suitable precursor for codoping but not for growing bulk fluoride films [68].

### 4.2 Metal precursors

#### 4.2.1 Halides

Metal halides, especially chlorides, are applicable precursors in ALD deposition of oxide, sulfide and nitride films. They are volatile and reactive enough but most of them are solids which is in microelectronic industry considered as a disadvantage. The ALD surface chemistry of chlorides has been studied thoroughly both on planar substrates and on high surface area oxide powders in preparation of oxides. As described above in those cases metal chlorides are reacting with surface OH groups and HCl is formed. Much less is known about the chemisorption on sulfur surfaces. The calculations show that  $\text{ZnCl}_2$  adsorbates on sulfur surface form a stable complex [54,55] though desorption of  $\text{ZnCl}_2$  may occur easily [56]. Due to the size of the chlorine anions and their repulsion, maximum surface coverage can be either  $1/3$  or  $1/2$  depending on whether the adsorption mode is independent or chain-like, respectively. Experimentally it has been shown that 2-3 cycles are needed for one monolayer depending on the experimental conditions [69]. The role of surface SH groups has not been studied in detail.

The behaviour of aluminium, gallium and indium trichlorides in the growth of oxide films differs from each other markedly:  $\text{Al}_2\text{O}_3$  can be grown with a good rate,  $\text{Ga}_2\text{O}_3$  does not grow at all,  $\text{In}_2\text{O}_3$  grows with a low rate. The oxide formation reactions become thermodynamically more unfavored in the same order. Partially those behaviours can possibly be addressed to the stability of OH groups on the oxide surface. The reactions of Al, Ga and In chlorides with ammonia follows the same trend as that with water. In GaAs ALE  $\text{GaCl}_3$  has been more often studied as a precursor than  $\text{GaCl}$ . The reaction between  $\text{GaCl}$  and  $\text{AsH}_3$  is not very favorable and long pulsing times are needed, and on the other hand  $\text{GaCl}$  desorption may occur and  $\text{GaCl}$  surface may change to inert Ga surface [70]. The studies have shown that  $\text{GaCl}_3$  reacts with  $\text{As}_2$  precursor only in the presence of hydrogen [71]. A rather wide 1 ML/cycle ALE window has been found for  $\text{GaCl}_3$ ,  $\text{AsH}_3$  and the suggestion for the reaction mechanism goes via AsH and As- $\text{GaCl}_2$  surface species [72].

$\text{SiCl}_4$  reacts with water producing  $\text{SiO}_2$  films. The reaction is, however, very slow and pulse times of tens of seconds are needed. The process relies on the surface OH groups and the growth rate is dependent on temperature which further determines the OH content on the surface [73]. The reaction can be enhanced by pulsing pyridine after each reactant pulse. Both the reaction temperature and pulse times could be reduced significantly without losing the growth rate per cycle and the quality of the film [74].

#### 4.2.2 Alkyl compounds

Because of the importance of the III-V semiconductors most ALE and ALD studies using alkyl precursors deal with Ga, Al and In. Both trimethyl and triethyl compounds are easily available and their chemistry in CVD is known. No special precursor for ALE has been designed. The ALE deposition of GaAs has been studied by numerous groups using different experimental set-ups and very different results have been reported. The difficulties arise from the instability of Ga alkyl compounds (mainly trimethyl gallium, TMGa). In ultra high vacuum systems no saturative growth or a very narrow temperature range for the saturation



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at with water. In GaAs ALE  $\text{GaCl}_3$  has  
between  $\text{GaCl}_3$  and  $\text{AsH}_3$  is not very  
 $\text{GaCl}_3$  desorption may occur and  $\text{GaCl}_3$   
that  $\text{GaCl}_3$  reacts with  $\text{As}_2$  precursor  
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he ALE deposition of GaAs has been  
and very different results have been  
nds (mainly trimethyl gallium, TMG)  
temperature range for the saturation

has been observed but the saturation can be enhanced by laser irradiation [45]. The use of high-speed flow  
in a hydrogen transport has resulted in reasonably wide saturation range [66,75].

Three models have been suggested for the ALE GaAs surface chemistry. First, the TMG converts the  
arsenic-terminated surface to a gallium-terminated one and the methyl groups desorb. This surface is no  
longer reactive towards TMG [76]. Second, TMG reacts with arsenic surface and forms a gallium rich  
surface covered with methyl groups. The methyl groups make the surface passive for further adsorption of  
TMG [77]. Third, TMG (or TEG) decomposes on the surface to a monomethyl (ethyl) species which desorbs  
from the surface and no deposition takes place. The growth requires a flux balance between the adsorbing  
and desorbing species [78]. As a conclusion it can be said that ideal saturative growth is hard to achieve by  
TMG (TEG) and arsine.

The behaviours of Al and In alkyls are similar to those of gallium alkyls in the growth of the III-V  
compounds. AlAs and InP are the most commonly studied materials after GaAs. By using different tricks  
in time scales, flow rates, precursor cracking, and  $\text{H}_2$  purges it has been possible to grow these materials 1  
ML/cycle in a limited temperature range [45]. In the growth of oxide films the alkyl compounds behave like  
chlorides:  $\text{TMA} + \text{H}_2\text{O}$  is almost an ideal reaction [79,80],  $\text{TMG} + \text{H}_2\text{O}$  does not proceed at all and  $\text{TMI}$   
 $+ \text{H}_2\text{O}$  shows extremely low growth rate [34]. TMA-water process works in a wide temperature range  
(100-500 °C) but the OH (or H) content of the film increases with decreasing temperature. The process has  
been studied in many applications including modification of catalyst supports and membranes [81], dielectric  
films for EL devices and corrosion protection films. The reaction of Al and Ga alkyl compounds with  
ammonia results in AlN and GaN [60,62]. Clear temperature window for the self-limiting growth does not  
exist but stable growth can be achieved at fixed temperature.

Dimethyl (DMZ) and diethyl (DEZ) zinc have been used in deposition of both epitaxial ZnS and ZnSe  
films as well as polycrystalline ZnS and ZnO films. Close to 1 ML/cycle growth was observed in the reaction  
between DMZ and  $\text{H}_2\text{S}$  at 25-500 °C [82]. The process can also be used in a large scale to fabricate ZnS:Mn  
based EL devices [83]. Both DMZ and DEZ react vigorously with water forming ZnO at 100-250 °C the  
ALD growth rate being reaction temperature dependent [84]. This and the observation that the reactions  
between DMZ and  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$  are hydrogen pressure dependent indicate thermal instability of the zinc  
alkyl compounds, not to forget the role of surface OH, SH and SeH groups, however. If the decomposition  
is complete and a zinc surface is formed, the chalcogenide formation reaction is inhibited.

#### 4.2.3 Alkoxides

Alkoxides which are well known precursors in CVD have only in a few cases used in ALD (Table 1) to grow  
oxide films. Water and alcohols have served as oxygen precursors [21,53]. Alkoxides have a tendency to  
decompose at high temperatures and therefore ALD processes are limited to temperatures below 400 °C  
where the growth is an ALD-type exchange reaction utilizing surface OH groups. The size of the precursor  
molecules affects the growth rate and in the case of  $\text{TiO}_2$  the precursor affects also the crystallinity [21,85].  
Alkoxides are very important precursors for Nb and Ta oxides because their chlorides etch the forming  
oxides [86,87].

#### 4.2.4 $\beta$ -diketonato complexes

Electropositive metals have not many volatile compounds and  $\beta$ -diketonato complexes are among the few  
ones. The need of volatile alkaline earth and rare earth metal compounds for CVD deposition of high  
temperature oxide superconductors boosted the studies on  $\beta$ -diketonato complexes. In ALD the main  
interest has been in deposition of Sr based EL phosphors and thd-chelates (Hthd = 2,2,6,6-tetramethyl-3,5-  
heptanedione) are used as the precursors [88]. The instability of the precursors may cause some thickness  
non-uniformity for the films and the difficulties increase in the series  $\text{Ca} < \text{Sr} < \text{Ba}$  [89]. Anyway,  $\text{Sr}(\text{thd})_2$  is  
used in a pilot scale for SrS EL films [90].

The alkaline earth  $\beta$ -diketonato complexes may oligomerize which limits the volatility and therefore neutral adducts have been added to the complexes to keep them monomolecular. The complexes may be aged by reacting with moisture also resulting in oligomers. The adduct molecules are believed to protect against aging as well [47,91]. ALD depositions of alkaline earth sulfide films have been carried out using adducted thd complexes but it seems that the neutral adduct molecules do not stay intact at growth temperatures [92,93]. Thus the surface reaction is basically the same as in the case of non-adducted complexes. One other way to avoid the aging and possible decomposition of the  $\beta$ -diketonato complexes is to make them *in situ* in the ALD reactor. This is possible by introducing Hthd liquid vapor over heated alkaline earth metal or hydroxide and a reasonable growth rate (0.8-1 Å/cycle) can be achieved [94]. The vaporization of the Hthd liquid inside the ALD reactor requires careful temperature control but this can be avoided by pulsing Hthd from outside of the ALD reactor [95].

As mentioned above the ALD deposition of oxide films from  $\beta$ -diketonato complexes and water is not a favourable reaction the deposition of MgO being an exception but with a low deposition rate [96]. The best results have been obtained by using ozone as an oxygen precursor. Even ternary  $\text{LaCoO}_3$  and  $\text{LaNiO}_3$  which usually are difficult to prepare by CVD techniques have been grown by ALD from the corresponding  $\beta$ -diketonato complexes and ozone [97,98].

$\text{Cu}(\text{thd})_2$  is a possible precursor for deposition of metallic copper. The reduction is made by  $\text{H}_2$  and due to the instability of the precursor the process is self-limited only in the temperature range 190 to 260 °C. The initiation of the growth is not straightforward and a Pt/Pd seed layer is needed [99,100].  $\text{Cu}(\text{thd})_2$ , as well as many rare earth thd-chelates have been employed as precursors for doping ZnS or SrS based EL phosphor films [101].

The adsorption of several transition metal thd-complexes on high surface area powders have been studied in detail [102]. In adsorption on oxide surface the thd-chelate undergoes an exchange reaction between the surface OH groups. The number of metal atoms on the surface is a function of the OH group concentration (calcination temperature) and the size of the molecule. There is one recent example of molecular adsorption of a  $\beta$ -diketonate chelate on silica surface, viz.  $\text{Cr}(\text{acac})_3$  (Hacac = 2,4-pentanedione). The molecular adsorption occurs only at a limited temperature range 160-200 °C, however [103].

#### 4.2.5 Cyclopentadienyl compounds

Magnesium and few other cyclopentadienyl (Cp) compounds are known as oxide precursors in CVD. Also some metal films have been grown by CVD from the cyclopentadienyl compounds. In ALD the first report on these precursors is that of Huang and Kitai [104] on MgO films. Our interest towards the Cp compounds stems from the need to find volatile compounds for the heavier alkaline earth metals capable to react with water to oxide at reasonable temperatures. Because the experiments with  $\beta$ -diketonates failed Cp compounds, though considered to be very sensitive to oxygen and moisture, were chosen. In practice however, these compounds turned out to be more stable than expected and could even be shortly exposed to air. Not much attention has been paid on the growth of binary oxide ( $\text{SrO}$ ,  $\text{BaO}$ ) films but more importantly ternary  $\text{SrTiO}_3$  and  $\text{BaTiO}_3$  compounds were grown with Ti alkoxide as a titanium source. The depositions on glass substrate follow the principles of ALD: the films are polycrystalline, the composition can be affected by changing the pulse ratio of the metal precursors, thickness is uniform and depends linearly on the number of the growth cycles, and the conformality of the films is perfect [105]. Cp compounds form a big family of precursors since the ligands can be varied by substitutions in the carbon 5-ring, enlarging the ring system (indene, fluorene) and by linking two ring systems together by a bridge. The potential of the Cp compounds as precursors for alkaline earth metals is still largely unknown. Metallocenes of the group 4 metals (Ti, Zr, Hf) are well-known in polyolefin catalysis and they are volatile compounds which react readily with water. Thus, these are also potential ALD precursors for  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$  films.

$\text{Sr}(\text{i-prop})_2\text{Cp}_2$  reacts also with  $\text{H}_2\text{S}$  forming SrS film. The benefit of this precursor is that temperatures below 200 °C can be used to fabricate crystalline films with high growth rates [106]. In luminescent EL films



erize which limits the volatility and therefore them monomolecular. The complexes may also. The adduct molecules are believed to protect earth sulfide films have been carried out using adduct molecules do not stay intact at growth ly the same as in the case of non-adducted decomposition of the  $\beta$ -diketonato complex in r. This is possible by introducing Hthd ligand. Reasonable growth rate (0.8-1 Å/cycle) can be in ALD reactor requires careful temperature of the ALD reactor [95].

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a dopant is needed and when an organometallic precursor for the dopant is a necessity, the growth temperature must be low and then the alkaline earth Cp-precursors may be a good choice.

Rare earth metals form another group of electropositive metals which have only a few volatile compounds. The rare earth  $\beta$ -diketonates are reasonably stable and their volatility properties are good but their reactivity with water to oxide films is low. As dopant precursors for  $\text{ZnS:Ln}$  and  $\text{SrS:Ln}$  films they can be used [101]. However, with cerium, one of the most important dopants for SrS, better results have been obtained with Cp precursors [83].

#### 4.2.6 Carboxylato complexes

The number of known volatile carboxylato complexes is low. In ALD only zinc acetate has been used in deposition of ZnS films [107]. Zinc acetate oligomerizes to a tetramer before evaporation and the actual molecule adsorbing on the surface is  $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$  and accordingly the growth rate of the film is high [106,108]. Zinc acetate can be used also as a precursor for ZnO films although the growth rate is very low.

#### 4.2.7 Silanes and germanes

ALE deposition of silicon (and also germanium) using different silanes or chlorosilanes has extensively been studied. Special attention has been given to the adsorption of different precursors on Si surface [19,20]. The results show that the surface chemistry of the precursors used is not favourable but UV-irradiation or thermal cycling is needed for obtaining pure films. According to Gates [109] all reactions studied in ALE using two Si precursors, silane + chlorosilane, are thermodynamically unfavoured. Only those reactions which involve atomic hydrogen are spontaneous and can be considered self-limiting. It seems that reactants which can be alternately pulsed and which make the self-limiting Si growth possible are not yet known.

#### 4.2.8 Others

There are few other precursors not mentioned above which have been used in ALD. Alkylamides, recently widely studied in CVD, have only a few times been used in ALD [110]. Isocyanate compounds of silicon ( $\text{Si}(\text{NCO})_4$ ) form a new interesting group of precursors with which it is possible to grow  $\text{SiO}_2$  films in a ML/cycle fashion [111,112]. The pulse times have, however, been unpractical long like in the case of  $\text{SiCl}_4$ . The development of these new precursors shows that new potential ALD precursors can be found.

### 5. FUTURE CHALLENGES

There are a lot of challenges and development work to be done before ALD is accepted as an important thin film deposition technology for opto- and microelectronics. As pointed out above the key role in the process development is the precursor chemistry. The first challenge is to get more chemists to work with the precursors. CVD faces the same challenge because worldwide the precursor development is not very extensive. On the other hand, there are of course more companies specializing on CVD precursors than ALD precursors. Luckily, these companies have shown increasing interest towards ALE and ALD which is a natural development recognizing the similarities of the two fields.

The areas where ALD precursor development is needed are obvious: areas where the experiments with chemicals available have not been very successful, viz. III-V compounds and silicon. The other areas where

precursor development is needed are at least: good reducers for reactions where oxidation states must be lowered, more efficient nitrogen source material than ammonia, new organometallic precursors for electropositive elements, stable volatile precursors for noble metals, and suitable reactant combinations for metal film depositions.

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